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⑮ 発明の名称 光酸化還元法

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⑱ 発 明 者 久 米 真 芦屋市朝日ヶ丘町1~27~310
⑲ 発 明 者 伊 熊 敏 郎 尼崎市武庫之荘東2~18~8
⑳ 出 願 人 日本板硝子株式会社 大阪市東区道修町4丁目8番地
㉑ 代 理 人 弁理士 大野 精市

明 細 書

1. 発明の名称

光酸化還元法

2. 特許請求の範囲

(1) 半導体微粒子と溶液とを接触させた反応系に光を照射させて酸化還元反応を起こさせる光酸化還元法において、光ファイバーの端面に半導体微粒子を担持せしめて半導体微粒子つき光ファイバーとし、該半導体微粒子つき光ファイバーを溶液と接触させた後該光ファイバーを通して光ファイバー端面の反応系に光を照射することを特徴とする光酸化還元法。

(2) 該光ファイバーがスタップ形又はグレーデッド形光ファイバーであり、該光ファイバーの開口角又は開口角よりもわずかに大きな入射角で該光ファイバーに光を入射させる特許請求の範囲第1項記載の光酸化還元法。

3. 発明の詳細な説明

(産業上の利用分野)

本発明は、半導体微粒子を用いた光酸化還元法に関し、特に効率の良い光酸化還元法に関する。

(従来技術)

近年、微粒子光触媒に関する研究が急速に発展している。これは光エネルギーを酸化チタン(TiO_2)、硫化カドミウム(CdS)などの半導体微粒子に吸収させ、生じた電子、正孔を用いて水分子(またはプロトン)を還元させたり、水又は有機物を酸化させる方法である。(例えばTrigger 1983年11月号、47~53頁)

従来、上記光酸化還元法の反応進行のための光の照射方法としては①ビーカー、フラスコ等の容器に半導体微粒子および溶液を入れ半導体微粒子が底に沈殿した状態で光を照射する方法、②上記反応液を攪拌させ半導体微粒子を溶液中に浮遊させた状態で光を照射する方法、③多孔質ガラス体に半導体微粒子を担持させ溶液に沈めて光を照射する方法。(例えば産業協会昭和58年度年会予稿集375~376頁(HJ2))等が知られている。

(発明が解決しようとする問題点)

上記光酸化還元法において、①の方法は有効な触媒が光の当る面上に覆われ低効率であり、②の方法は光が触媒微粒子により散乱されて系外に失われたり、又溶液自体に光吸収性又は散乱特性のある場合、有効に光照射が行なわれず効率が悪くなる欠点があった。又③の方法でも、光照射に参与する触媒が多孔体の光の当る表面近傍のものに限られ、かつ②と同様、溶液自体に光吸収性又は散乱特性のある場合は効率が悪くなる欠点があった。

本発明は従来の光酸化還元法よりも効率の良い光酸化還元法を提供することをその目的とし、特に吸光特性を持つ溶液又は散乱を多くおこす溶液について反応進行が難しかった従来法の問題点の解決をはかるものである。

(問題点を解決するための手段)

上記問題点を解決するために、本発明は光ファイバーの端面に半導体微粒子を担持せしめて半導体微粒子つき光ファイバーとし、該半導体微粒子つき光ファイバーを溶液と接触させた後、該光フ

ないものが好まれる。

本発明によれば、光ファイバーに光を入射させることによって光ファイバーを介して反応系に光を導くことができるが、光ファイバーに対する光の入射方法として①その光ファイバーの開口角の近傍、特に開口角よりもわずかに大きな角度でファイバーに光を入射させる方法(光ファイバーとして通常の光ファイバーを使用した場合に有効)②適当な角度(開口角内)でファイバーに光を入射させる方法(散乱損失の非常に大きいファイバーを用いた場合に有効)などがあげられる。

又本発明によれば、反応に参与できる反応系の表面積も、反応容器内に充填される半導体微粒子つき光ファイバーの本数を増加することによって容易に広げられる。

以下に本発明を実施例に基きさらに詳細に説明する。

(実施例)

まず特設試験の TiCl_4 を加水分解させて TiO_2 溶液で 2.27g/ml の TiO_2 ヒドロゾル溶液

ファイバーを通して半導体微粒子と溶液とからなる反応系に光を照射することを特徴とする光酸化還元法を提供する。

本発明に使用する光ファイバーはガラス製、プラスチック製等任意の材質のもの、任意のファイバー特性(ステップ形、グレーデッド形、その他)のもの、任意の太さのもの(例えば直径 25 μm ~ 1mm のもの)が使用できる。内でも連続的に太さが増加している様な形状欠陥による光の散乱(もれ)損失の大きな光ファイバ、中心および周囲の屈折率差が小さく、散乱(もれ)損失の大きな光ファイバ等が好まれる。

又本発明で用いる半導体微粒子は、 TiO_2 、 MoS_2 、 SrTiO_3 、 CdS 、 GaP 、 In_2O_3 、 H_2O_2 などの可視光で水-エタレールからの水素発生に活性である半導体微粒子の他、光による酸化還元反応に対して活性な半導体微粒子である。

光ファイバーに半導体微粒子を担持させる方法としては通常の固定方法が使用できるが、内でも担持により反応系に照射される透過光の減少の少

100ml を作製した。この溶液に 1 モル/l の NH_4OH 溶液を中和するまでゆっくりと攪拌しながら加え、さら 1 wt% の $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ 溶液を 2ml、同じく 1 wt% の $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ 溶液を 1ml 加えた。この溶液中にコア径 150 μm 、外径 200 μm 、長さ 10cm の開口角 15° の製グレーデッドインデックス型 GeO_2 - SiO_2 系光ファイバー(1)を多数浸漬させた。その後該ファイバー(1)を溶液より引きあげ、100°C、30分乾燥後、300°C で 1 時間熱処理して半導体微粒子つき光ファイバー(3)とした。

ここで該ファイバーの表面には 0.2 ~ 1 μm の厚みの半導体微粒子からなるコーティングが形成されていた。

こうして作成した半導体微粒子つき光ファイバー(3)を用いて、第 1 図に示す様な光酸化還元装置を以下の手順で作成した。

まず、前記方法で作成した多数の半導体微粒子つき光ファイバー(3)を、その一端を反応容器の蓋(4)に気密性を保ちながら固定してつり下げる。ここで蓋(4)には光酸化還元反応により反応系より発

生した H_2 ガスを排出するためのガス排出口(5)が設けられている。そして該光ファイバー(3)つき蓋(4)を、溶液注入口(6)および溶液排出口(7)つき反応容器(8)に気密状態に取り付け、該反応容器上方に500W高圧水銀灯(9)および集光用の凸レンズ(10)を設けた。

ここで蓋(4)に対する半導体微粒子つき光ファイバー(3)の取り付け位置、高圧水銀灯(9)の位置および集光用凸レンズ(10)位置は、水銀灯(9)より照射した光が半導体微粒子つき光ファイバー(3)に該ファイバーの開口角(15°)よりもわずかに大きな入射角で入射する様位置関係を調整されている。

該光酸化還元装置を用い、反応容器(8)内に $30^\circ C$ の CH_3OH 濃度25モル%の CH_3OH-H_2O 混合液(11)250mlを満たすと共に同混合液を25ml/時の速度で溶液注入口(6)から注入し同排出液を溶液排出口(7)から排出した。高圧水銀灯(9)を点灯することにより溶液から H_2 ガスが発生しガス排出口(5)より約2000ml/時の H_2 ガス($0^\circ C$ /atm)が捕集された。

(比較例)

実施例と同様に作成した $TiO_2-Pt-RuO_2$ 系のヒドロゾル混合溶液に、平均孔径20~30 μm のガラスフィルターを浸して細孔中に混合溶液を含ませ、実施例と同様に乾燥、熱処理して、半導体微粒子つきガラス多孔質体(12)を作成した。

こうして作成した半導体微粒子つきガラス多孔質体(12)を第2図に示す様な光酸化還元装置へ充填した。第2図において反応容器(13)は溶液追加用タンク(14)、温度計(15)、気体捕集用管(16)、反応液だめ部(17)からなる。反応液だめ部(17)の底面積は約30 cm^2 であり、反応液だめ部の下方には下方より光を照射するためのHgランプ(9)およびレンズ(10)が設けられている。

反応液だめ部に実施例/と同様 $30^\circ C$ 、25モル%濃度の CH_3OH-H_2O 混合液を250ml調しした後、反応液だめ部(17)の下方より500Wの水銀灯(9)の光を照射した所約245ml/時の H_2 ガス($0^\circ C$ /atm)が捕集された。

ここで反応液だめ部に充填された半導体微粒子

ここでファイバー表面に担持された半導体微粒子の重量を装置に使用されたファイバー本数および半導体微粒子つきファイバー(3)作成時の溶液の減量から推定し、 H_2 ガスの発生効率を求めると約4000ml/hour $\cdot g TiO_2$ ($0^\circ C$ /atm換算)となった。

本実施例によれば、水銀灯より発生した光が蓋(4)に固定された半導体微粒子つき光ファイバー(3)にファイバーの開口角よりもわずかに大きな入射角で入射し、光ファイバー内を進行した後ファイバー端面の半導体微粒子に照射される。そこで本実施例によれば光が半導体微粒子に照射されるまでの間に溶液内を通過することがない。つまり溶液による光の吸収、散乱の心配がない。又本実施例では光ファイバーとして GeO_2-SiO_2 系の光ファイバーを用いているためファイバー表面の耐酸性が良好であり光酸化還元用溶液に対して非常に安定である。

次に本発明の効果を明らかにするために、従来法を比較例として以下に説明する。

つきガラス多孔質体の重量および作成時の条件よりガラス多孔質体に担持された半導体微粒子の重量を推定し、 H_2 ガスの発生効率を求めると約490ml/hour $\cdot g TiO_2$ ($0^\circ C$ /atm換算)となった。

又上記半導体微粒子つきガラス多孔質体(12)のかわりに TiO_2 微粒子0.5gを用い同装置で同様に光照射を行なった所 H_2 ガス発生効率は50ml/hour $\cdot g TiO_2$ ($0^\circ C$ /atm換算)となった。

又上記装置の反応液だめ部(17)に攪拌装置を設け攪拌を行ないながら上記 TiO_2 微粒子0.5gを用いて光照射を行なったところ H_2 ガス発生効率は16ml/hour $\cdot g TiO_2$ ($0^\circ C$ /atm換算)となった。

上記比較例から明らかな通り、本実施例では従来法と較べて高率な酸化還元反応が行なわれていたことがわかる。

(発明の効果)

本発明によれば、実施例からもあきらかな通り従来法とくらべて効率の良い H_2 発生が行なえる光酸化還元法である。特に本発明によれば、溶液内

に光を透過させて光酸化還元を行なわせていた従来法では効率が悪かった溶液自体に吸光特性を持った溶液、散乱を多くおこす溶液を用いても効率良く光酸化還元が行なえるものである。

図面の簡単な説明

第1図は本発明の光酸化還元法を実施するための光酸化還元装置の概略説明図であり、第2図は従来法の光酸化還元を実施するための光酸化還元装置の概略説明図である。

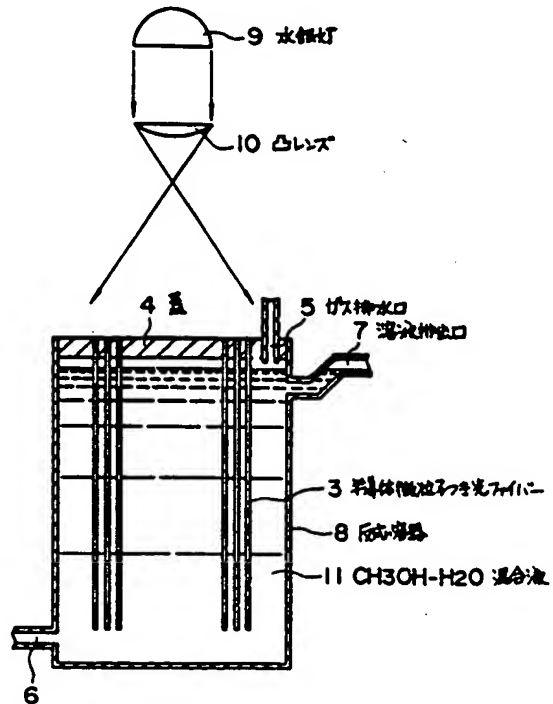
- (3) 半導体微粒子つき光ファイバー
- (4) 水銀灯
- (9) 水銀灯 (10) レンズ
- (11) $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ 混合溶液
- (12) 半導体微粒子つき多孔質ガラス

特許出願人 日本板硝子株式会社

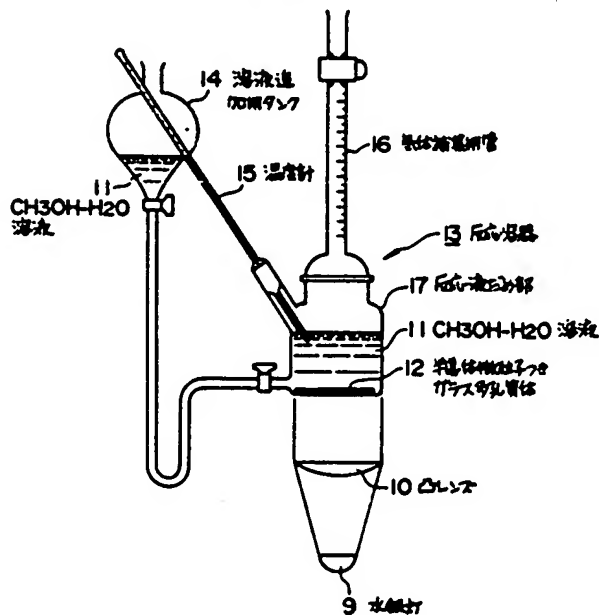
代理人 弁理士 大野 精 市



第 1 図



第 2 図



Japanese Kokai Patent Application No. Sho 61[1986]-97102

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PHOTOREDOX METHOD

Inventors:	Makoto Kume 1-27-310 Asahigaoka-machi, Toya-shi Toshiro Ikuma 2-18-8 Mukonosohigashi, Amagasaki-shi
Applicant:	Nippon Ita Garasu K.K. 4-8 Doshu-machi, Higashi-ku, Osaka
Agent:	Kiyoichi Ono, patent attorney

[There are no amendments to this patent.]

Claims

1. A photoredox method whereby the redox reaction is brought about by bringing semiconductor microparticles and a solution into contact and irradiating the reaction system with light, said photoredox method being characterized in that the semiconductor microparticles are

carried on the side surfaces of optical fibers, thus producing optical fibers with attached semiconductor microparticles, and after bringing said optical fibers with attached semiconductor microparticles into contact with a solution, the reaction system at the side surfaces of the optical fibers is irradiated with light that passes through said optical fibers.

2. The photoredox method according to Claim 1, wherein said optical fiber is a step-index or graded-index optical fiber, and light is made to impinge on said optical fibers at an angle of incidence that is slightly greater than the [illegible] angle or aperture angle of said optical fiber.

Detailed explanation of the invention

Industrial application field

The present invention relates to a photoredox method that employs semiconductor microparticles and, in particular, relates to a photoredox method that has good efficiency.

Prior art

Research regarding microparticulate photocatalysts is experiencing rapid development. For example, there is a method whereby light energy is absorbed by semiconductor microparticles such as titanium oxide (TiO_2) or cadmium sulfide (CdS), and the electrons or holes generated thereby are used in order to reduce water molecules (or protons), thereby causing the oxidation of water or organic substances (e.g., Trigger, November 1983, pp. 47-53).

Examples of past photoirradiation methods carried out in order to accelerate the reactions in the aforementioned photoredox methods include (1) methods involving the introduction of semiconductor microparticles and a solution into a beaker, flask or other such container, and subsequent irradiation of the material with light wherein the semiconductor microparticles have sedimented at the bottom of the container, (2) methods involving stirring the aforementioned reaction liquid in order to suspend the semiconductor microparticles in the solution, followed by irradiation of the material with light with the particles in this state, and (3) methods involving supporting the semiconductor microparticles on a porous glass body, and subsequent irradiation of the material with light with this material immersed in a solution (for example, see [illegible] Industry Association 1983 Letters No. 375-376 (H32)).

Problems to be solved by the invention

Among the aforementioned photoredox methods, the methods presented in (1) are low-efficiency methods in which effective catalyst is restricted to the catalyst at the surface on which light impinges. With the methods presented in (2), the light can be scattered by the catalyst microparticles and lost from the system, or the solution itself can have characteristics whereby it absorbs or scatters light. In such case, there is the disadvantage that the efficiency is

poor, because irradiation with light cannot be effectively brought about. With the methods presented in (3), the catalyst that is irradiated with light is restricted to material near the surface of the porous body on which the light impinges, and as in (2), there is the disadvantage of poor efficiency when the solution itself has characteristics whereby it absorbs or scatters light.

The present invention has the objective of offering a photoredox method that has better efficiency than conventional photoredox methods and, in particular, has the objective of solving problems with conventional methods in regard to stimulating reactions in solutions that have characteristics that cause them to absorb or significantly scatter light.

Means to solve the problems

In order to solve the above problems, the present invention offers a photoredox method characterized in that semiconductor microparticles are supported on the side surfaces of optical fiber to produce optical fibers with attached semiconductor microparticles, and after bringing said optical fibers with attached microparticles into contact with a solution, light is made to irradiate the reaction system comprising the solution and the semiconductor microparticles via said optical fibers.

The optical fibers used in the present invention can be made from glass, plastic or any other material, and can have any fiber characteristics (step-form, graded or other) and any thickness (for example, materials of diameter 25 μm to 1 mm). Preferred among these materials are optical fibers that have large scattering loss (leakage) of light due to morphology defects and a thickness that varies continuously, and optical fibers that have a difference in index of refraction between the center and periphery, and which also have large scattering loss (leakage).

The semiconductor microparticles used in the present invention are semiconductor microparticles that are active in terms of generating hydrogen from water-ethanol under the influence of visible light. Examples include TiO_2 , SrTiO_3 , CdS , GaP , In_2O_3 , and MoS_2 . Other such particles are semiconductor microparticles that are active in terms of redox reactions brought about by light.

The method for supporting the semiconductor microparticles on the optical fiber can be a common fixing method, but among such methods, those are preferred whereby supporting of the material causes little attenuation of transmissive light that is used to irradiate the reaction system.

In the present invention, light can be conducted into the reaction system via the optical fiber by making the light impinge upon the optical fiber. Examples of methods for bringing about impingement of light on the optical fiber that may be cited include (1) methods wherein light is made to impinge on the optical fiber at an angle that is close to the aperture angle of the optical fiber, and in particular, at an angle that is slightly larger than the aperture angle (effective when ordinary optical fiber is used for the optical fiber), and (2) methods wherein light is made to

impinge on the optical fiber at an appropriate angle (smaller than the aperture angle; effective when an optical fiber is used that has extremely high scattering loss).

By means of the present invention, the surface area of the reaction system that can participate in the reaction is readily increased by increasing the number of optical fibers having affixed semiconductor microparticles that are loaded into the reaction vessel.

The present invention is described in additional detail below.

Application example

First, special reagent-grade TiCl_4 was hydrolyzed to produce 100 mL of TiO_2 hydrosol solution with a concentration of 2.274 mol/L based on TiO_2 . 1 mol/L NH_4OH solution was then added slowly to this solution while stirring in order to effect neutralization, and 2 mL of 1 wt% $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ solution and 1 mL of 1 wt% $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ solution were added. Multiple strands of quasi-graded index GeO_2 - SiO_2 system optical fiber (1) having a core diameter of 150 μm , an external diameter of 200 μm , a length of 10 cm and an aperture angle of 15° were then immersed in this solution. Subsequently, said fiber (1) was removed from the solution, dried for 30 min at 100°C , and thermally treated for 1 h at 500°C to produce optical fiber (3) with attached semiconductor particles.

By this means, a coating composed of semiconductor microparticles was formed on the surface of said fibers at a thickness of 0.2-1 μm .

Optical fibers (3) with attached semiconductor microparticles produced in this manner were used, and a photoredox device of the type shown in Figure 1 was produced by the following procedure.

First, multiple optical fibers (3) having attached semiconductor microparticles produced by the above method were fixed at one end in the lid (4) of the reaction vessel so that air-tightness was maintained, and the fibers were allowed to hang. A gas discharge opening (5) was provided in the lid (4) in order to exhaust H_2 gas generated by the reaction system in the photoredox reaction. Then, the lid (4) having said optical fibers (3) was attached in an air-tight condition to a reaction vessel (8) having a solution discharge opening (7) and a solution introduction opening (6), and a 500 W high-pressure mercury lamp (9) and convex condensing lens (10) were installed above said reaction vessel.

The attachment position with respect to the lid (4) of the optical fibers (3) having attached semiconductor microparticles, the location of the high-pressure mercury lamp (9) and the location of the condensing convex lens (10) were adjusted to produce positional relationships such that the light emanating from the mercury lamp (9) was incident on the optical fibers (3) with attached semiconductor microparticles at an angle of incidence that was slightly larger than the aperture angle of said fibers (15°).

Said photoredox device was used, and the reaction vessel (8) was filled with 250 mL of a 30°C CH₃OH-H₂O mixed liquid (11) having a CH₃OH concentration of 25 mol%. Simultaneously, the same mixed liquid was introduced from the solution introduction opening (6) at a rate of 25 mL/h, and discharge liquid was also similarly discharged from the solution discharge opening (7). When the high-pressure mercury lamp (9) was turned on, H₂ gas was generated from the solution, and H₂ gas was collected at about 2000 mL/h (0°C, 1 atm) from the gas exhaust opening (5).

The weight of the semiconductor microparticles supported on the fiber surface was hypothesized from the decrease in the amount of solution during production of the fibers (3) with attached semiconductor microparticles and the number of fibers used in producing the device. The H₂ gas generation efficiency was then calculated to be about 4000 mL/h·g TiO₂ (0°C, 1 atm).

In this application example, the light generated by the mercury lamp was made to impinge upon the optical fibers (3) with attached semiconductor microparticles and fixed in the lid (4) and the angle of incidence was slightly larger than the aperture angle of the fiber. After traveling through the optical fiber, the light then impinged upon the semiconductor microparticles on the sides of the fibers. Thus, by means of this application example, the light did not pass through the solution in order to irradiate the semiconductor microparticles. In other words, there is no concern over absorption or scattering of light by the solution. Moreover, in this application example, the durability of the fiber surfaces is good because GeO₂-SiO₂ system optical fiber was used for the fiber, and the fibers are thus extremely stable with respect to the photoredox solution.

A conventional method is presented below using a comparative example in order to clarify the effects of the present invention.

Comparative example

A glass filter with an average pore diameter of 20-30 μm was immersed in a TiO₂-Pt-RuO₂ hydrosol mixed solution produced in the same manner as in the application example, so that the pores were infused with the mixed solution. The material was then dried and thermally treated in the same manner as in the application example, thus producing a glass porous material (12) with attached semiconductor microparticles.

The glass porous material (12) with attached semiconductor microparticles produced in this manner was then packed into the type of photoredox device shown in Figure 2. In Figure 2, the reaction vessel (13) comprises a solution replenishment tank (14), a temperature gauge (15), a gas collection line (16), and a reaction liquid reservoir (17). The bottom surface area of the reaction liquid reservoir (17) is about 30 cm². A Hg lamp (9) and lens (10) are provided to cause light to impinge from below on the bottom of the reaction liquid reservoir.

As in Application Example 1, the device was filled with 250 mL of a 30°C CH₃OH-H₂O mixed liquid having a [methanol] concentration of 25 mol%, and the bottom of the reaction liquid reservoir (17) was irradiated from below with light from a 500 W mercury lamp (9). As a result, 245 mL/h of H₂ gas was collected (0°C, 1 atm).

The weight of the semiconductor microparticles supported on the glass porous material was estimated based on parameters at the time of production of the device and the weight of the glass porous material with attached semiconductor microparticles packed into the reaction liquid reservoir. The H₂ gas generation efficiency was calculated to be about 490 mL/h·g TiO₂ (0°C, 1 atm).

The H₂ gas production efficiency was 50 mL/h·g TiO₂ (0°C, 1 atm) when 0.5 g of TiO₂ microparticles was used instead of the aforementioned glass porous material (12) with attached semiconductor microparticles and irradiation was carried out in the same manner using the same device.

A stirring device was attached to the reaction liquid reservoir (17) of the aforementioned device, and when irradiation was carried out using the above 0.5 g of TiO₂ microparticles while stirring, the H₂ gas generation efficiency was 16 mL/h·g TiO₂ (0°C, 1 atm).

As is clear from the above comparative example, the high-efficiency redox reaction occurring in the application example was higher in efficiency than that of the conventional methods.

Effect of the invention

It is clear from the application example that the present invention provides a photoredox method whereby H₂ is generated with better efficiency relative to conventional methods. In particular, by means of the present invention, photoredox is carried out with good efficiency, even when using a solution that causes significant scattering or a solution that has light-absorbing characteristics, which has caused poor efficiency in conventional methods in which photoredox has been carried out by passing light through the solution.

Brief description of the figures

Figure 1 is a schematic explanatory diagram of the photoredox device used for carrying out the photoredox method of the present invention. Figure 2 is a schematic explanatory diagram of a photoredox device used in order to carry out photoredox in a conventional method.

- 3 Optical fiber with attached semiconductor microparticles.
- 9 Mercury high-pressure lamp
- 10 Lens
- 11 $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ mixed solution
- 12 Porous glass with attached semiconductor microparticles

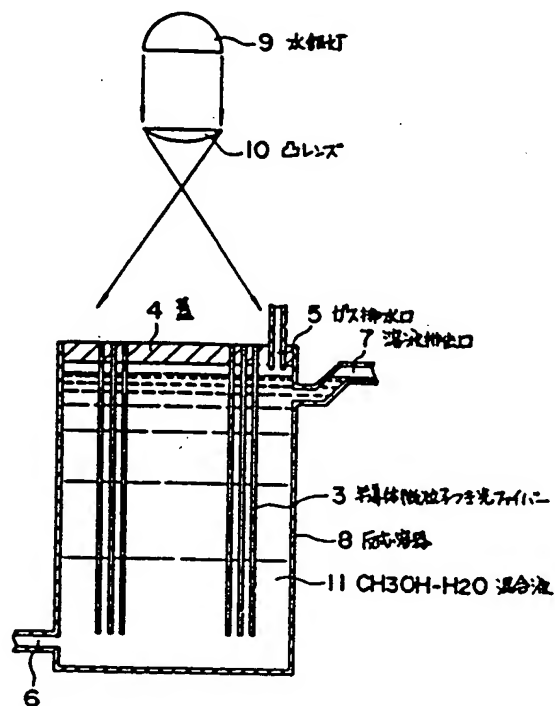


Figure 1

- Key:
- 3 Fiber with attached semiconductor microparticles
 - 4 Lid
 - 5 Gas exhaust opening
 - 7 Mixed liquid discharge opening
 - 8 Reaction vessel
 - 9 Mercury lamp
 - 10 Convex lens
 - 11 $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ mixed liquid

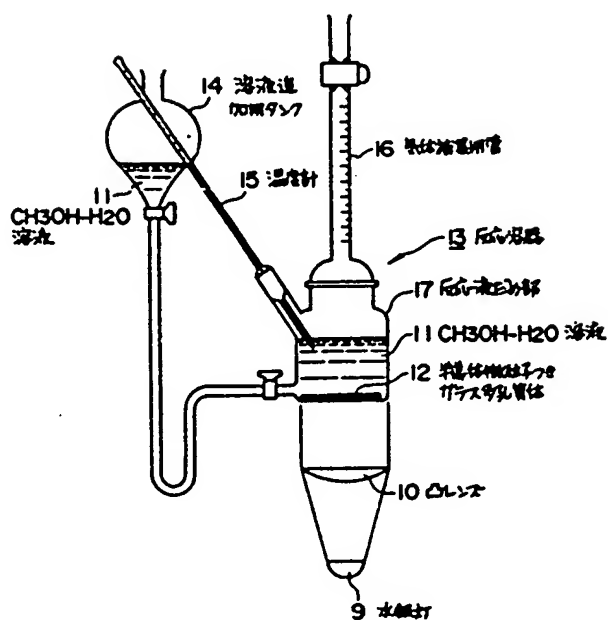


Figure 2

- Key:
- 9 Mercury lamp
 - 10 Convex lens
 - 11 $\text{CH}_3\text{OH}-\text{H}_2\text{O}$ solution
 - 12 Glass porous material with attached semiconductor microparticles
 - 13 Reaction vessel
 - 14 Solution replenishment tank
 - 15 Temperature gauge
 - 16 Gas collection line
 - 17 Reaction solution reservoir

